

Thermodynamic investigation and environment impact assessment of hydrogen production from steam reforming of poultry tallow



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ABSTRACT

In this research, various assessment tools are applied to comprehensively investigate hydrogen production from steam reforming of poultry tallow (PT). These tools investigate the chemical reactions, design and simulate the entire hydrogen production process, study the energetic performance and perform an environment impact assessment using life cycle assessment (LCA) methodology.

The chemical reaction investigation identifies thermodynamically optimal operating conditions at which PT may be converted to hydrogen via the steam reforming process. The synthesis gas composition was determined by simulations to minimize the Gibbs free energy using the Aspen Plus™ 10.2 software. These optimal conditions are, subsequently, used in the design and simulation of the entire PT-to-hydrogen process. LCA is applied to evaluate the environmental impacts of PT-to-hydrogen system. The system boundaries include rendering and reforming along with the required transportation process. The reforming inventories data are derived from process simulation in Aspen Plus™, whereas the rendering data are adapted from a literature review. The life cycle inventories data of PT-to-hydrogen are computationally implemented into SimaPro 7.3. A set of seven relevant environmental impact categories are evaluated: global warming, abiotic depletion, acidification, eutrophication, ozone layer depletion, photochemical oxidant formation, and cumulative non-renewable fossil and nuclear energy demand. The results are subject to a systematic sensitivity analysis and compared to those calculated for hydrogen production from conventional steam methane reforming.

The LCA results indicate that the thermal energy production process is the main contributor to the selected environmental impact categories. Improvement actions to minimize the reforming thermal energy and the transport distance are strongly recommended as they would lead to relevant environmental improvements.

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1. Introduction

Hydrogen (H_2) is regarded as the fuel for next generation and extensive research is being pursued for search of new and efficient techniques for H_2 production. According to Romm [1] there are two important pillars upon which the H_2 economy rests on: pollution-free sources for the H_2 production, and fuel cells for converting the H_2 to useful energy efficiently. Unfortunately, 95% of the current H_2 production comes from steam reforming of non-renewable natural gas [2]. H_2 derived non-renewable fuels will be either carbon intensive or expensive because of carbon sequestration costs. The expected increased demand for H_2 for fuel cell applications, however, dictates the development of new methods for eco-friendly H_2 production, especially from bio-renewable feedstocks. Therefore, the USA, Japan, China, India, and several European countries

have established research and development programs focused on renewable H_2 production and fuel cell technology to solve the energy problem and the high dependence on fossil fuels.

Currently, the industrial practices have led to the generation of an enormous amount of crude fatty materials (CFM) as waste, and these materials are difficult to treat and valorize [3]. One such material is tallow from slaughterhouses, meat industry and food industry waste. Tallow is a rendered form of beef, poultry or mutton fat, processed from suet. Like vegetable oils (VO), tallow is primarily composed of triglycerides, with minor amounts of mono and diglycerides. A triglyceride consists of a three-carbon glycerol head groups conjugated to three fatty acid chains [4]. All triglycerides have the same basic structure, and the differences in properties and use of commercial triglycerides depends entirely on the degree of unsaturation, length and other chemical modifications to the fatty acid chains [4]. The fatty-acid carbon-chain lengths vary between 4 and 24 carbon atoms with up to six double bonds.

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Nomenclature

ADP	abiotic depletion potential	PEI's	potential environmental impacts
AP	acidification potential	PEMFC	proton exchange membrane fuel cell
CED	cumulative non-renewable fossil and nuclear energy demand	POFP	photochemical oxidant formation
CFM	crude fatty materials	PT	poultry tallow
COPROX	carbon monoxide preferential oxidation	PT-to-H ₂	poultry tallow to hydrogen
EP	eutrophication potential	Q	heat duty
FU	functional unit	SB	system boundaries
GWP	global warming	SG	synthesis gas
HTS	High Temperature Shift	SMR	steam methane reforming
LCA	life cycle assessment	ST	steam reforming
LCI	life cycle inventory	S/C	steam to carbon ratio
LCIA	life cycle impact assessment	TBD	tallow-based biodiesel
LTS	Low Temperature Shift	VO	vegetable oil
LHV	Lower Heating Value	WGS	water gas shift
<i>m</i>	mass flow	η_{Thermal}	thermal efficiency
ODP	ozone layer depletion	$\alpha_{\text{H}_2, \text{ renewability}}$	hydrogen renewability ratio
<i>P</i>	pressure		

As an overview of the world's statistic, a total of 24.64 million tones of animal/oils (i.e. butter, lard, tallow, grease and fish oil) were produced in 2007 [5]. Considering this huge amount, the valorization of these renewable and cheap fatty materials remains necessary. The use of tallow as a food additive is declined due to changing feeding habits of people and the soap industry cannot take up all the excess animal fat produced. In the last years considerable attention has been paid to the use of tallow for the production of biodiesel and other oleochemicals [6–10]. Biodiesel fuels produced from tallow and VO have comparable compositions [11]. However, there are some differences; the main one is that the tallow-based biodiesel (TBD) contains more saturated fatty esters [11]. Tallow as a biodiesel feedstock has some advantages and disadvantages. TBD has a higher cetane number than VO biodiesel, which means that TBD is cleaner and burns more efficiently in diesel engines [4]. However, TBD has a higher cloud point because of the high levels of saturated fatty acids. Its higher cloud point means that TBD tends to crystallize out at low temperatures, creating problems in engines. Used pure (100%) TBD would not meet the European standards. However, when blended at about 5% into conventional diesel, the mixture meets the relevant fuel quality standards [12].

This paper explores an innovative application for valorization of poultry tallow (PT) for H₂ production via steam reforming (SR) process. In fact, we believe that PT is a promising feedstock for producing renewable H₂ because the O₂ content is low and the potential yield of H₂ is high. Moreover, tallow is a potential alternative for H₂ production due to the highly centralized generation in slaughter processing facilities and historically low prices; this may have energy, environmental, and economic advantages that could be exploited. H₂ obtained from tallow has been proposed to be a low-risk end use for tallow from livestock that are removed from the food chain [13,14].

Currently, life cycle assessment (LCA) is considered a systematic tool evaluating the environmental impacts occurring throughout the entire life cycle of a process, product, or activity [15–17]. LCA leads to insight into the overall system performance and the relative contributions of the different stages in its lifetime with the so-called cradle-to-grave approach. The results of LCA can be helpful for promoting sustainable development policy and increasing environmental awareness in public [18]. In recent years, LCA methodology has been specifically used in

environment assessment of new technologies for bioenergy including bioethanol [19,20], biomethanol [21], biomethane [22,23], biohydrogen [24,25]. Moreover it has been proven to be a valuable tool for analyzing energy and environmental considerations of CFM valorization. Dufour and Iribarren [26] performed a LCA of four biodiesel production systems including esterification–transesterification of waste VO (used cooking oil) and animal fats (beef tallow, poultry fat), and in situ transesterification of sewage sludges. They showed that biodiesel from waste VO potentially entailed the most favorable environmental performance and concluded that actions aimed at minimizing thermal and electric energy demands would lead to relevant environmental improvements. Morais et al. [27] compared the potential environmental impacts (PEI's) of three process design alternatives for biodiesel production from waste VO that are: the conventional alkali-catalyzed process including a free fatty acids pre-treatment, the acid-catalyzed process, and the supercritical methanol process using propane as co-solvent. They showed that the supercritical methanol process using propane as co-solvent is the most environmentally favorable alternative. The acid-catalyzed process generally shows the highest PEI's, in particular due to the high energy requirements associated with methanol recovery operations.

Djomo and Blumberga [25] applied the LCA methodology to quantify and to compare the energetic and environmental performances of H₂ from wheat straw, sweet sorghum stalk, and steam potato peels. They concluded that the energy ratios and the greenhouse gas emissions (GHG) of BioH₂ compared favorably with diesel and other fossil H₂ production pathways and the co-product yield is an important parameter when selecting a BioH₂ feedstock. Koroneos et al. [28] investigated the environmental aspects of H₂ production. They compared H₂ production methods with steam methane reforming (SMR) and five different renewable ways, which were solar energy using photovoltaic for direct conversion, solar thermal energy, wind power, hydropower and biomass. They cited that the use of wind, hydropower and solar thermal energy for the production of H₂ were the most environmental benign methods. Further investigation of hydrogen production system via LCA methodology was recently reported by Susmozas et al. [29]. The authors evaluated the environmental performance of H₂ production via indirect gasification of poplar biomass. They reported that the gasification-derived BioH₂ is generally a promis-

ing H₂ fuel, with reduced GHG and a low non-renewable energy demand.

In this research, various assessment tools are applied to comprehensively investigate PT to H₂ production system (PT-to-H₂). These tools investigate the chemical reactions system, design and simulate the entire H₂ production process, study the energetic performance and perform an environment impact assessment (using LCA methodology). The chemical reactions investigation identifies thermodynamically optimal operating conditions at which PT can be converted to H₂ via the SR. This part constitutes itself a key outcome of the present study. In fact, because of the complexity chemical composition of PT, the unavailability of physical and chemical properties and the multiplicity of chemical reaction occurred; thermodynamic investigation of H₂ production by SR of PT has not been considered in the past. The optimal conditions obtained are used in the design and simulation of an entire H₂ production process. The results from the process simulation were subsequently exploited as inputs data for life cycle inventory. Another innovative aspect of this investigation is the use, for the first time, of LCA methodology to a PT-to-H₂ system to get an overview of the environmental impacts associated with the life cycle of H₂ production. Indeed, LCA of biodiesel production from various CFM (VO and tallow) are already considered by many authors [26,27,30–32]. Although numerous studies have been conducted dealing with H₂ production from CFM [33–37] but, to the best of our knowledge, LCA of H₂ production from VO and/or tallow has not yet been published.

2. Hydrogen production by steam reforming of poultry tallow

2.1. Poultry tallow characterization

As described above, PT is primarily composed of triglycerides. Table 1 gives the typical fatty-acid composition of the PT considered in this work.

The lower heat value of PT is calculated by the equation of Demirbas [39] which is an empirical calculation based on chemical analysis data ($LHV_{PT} = 40.84$ MJ/kg).

In this paper, Aspen Plus™ 10.2 software (Aspen Technology, Inc., Burlington, MA, USA) [40] is used to investigate the chemical reaction system and to simulate the entire PT-to-H₂ process. Unfortunately, all triglyceride forms (given in Table 1) are not included in the Aspen Plus™ databank; they needed to be added before the simulation could be started. This operation required various data, such as normal boiling point, the chemical structure, temperature-dependent vapor pressures and heat capacity, molecular weight, standard enthalpy and Gibbs free energy of formation of these compounds, to be inserted into the Aspen Plus™ dialog box [40]. All data required for the regression of the property method are obtained from different open literatures sources [37,41,42].

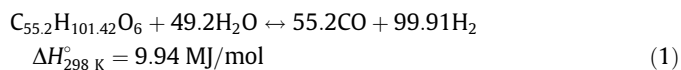
2.2. Steam reforming of poultry tallow

This section enabled the optimal operating parameters of SR of PT to be chosen for the simulation of the entire H₂ production process. The values of the operating parameters for the reactor must be chosen to maximize the H₂ production while minimizing the

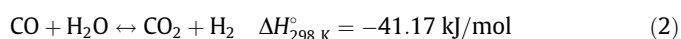
CH₄ and CO concentrations in the synthesis gas (SG). CH₄ is not converted into H₂ in the water gas shift reactors (WGS); therefore, higher levels of CH₄ result in lower H₂ yields. It is also important to reduce the CO concentration in the synthesis gas to reduce the required size of the gas-cleaning unit (WGS and COPROX).

SR of PT is an endothermic reaction in which the substrate is treated with steam in the presence of a catalyst to SG. The SR of an oxygenated hydrocarbon, such PT, involves a complex reaction system, with undesired reaction paths [2].

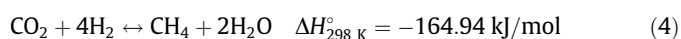
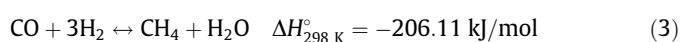
The main reactions concerned in the reforming process are:



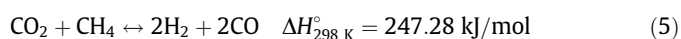
Water gas shift (WGS):



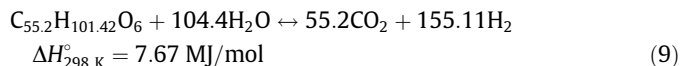
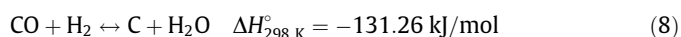
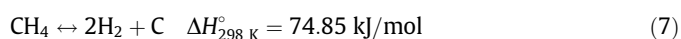
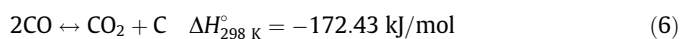
Methanation:



Methane CO₂ reforming:



Carbon formation:



This overall reaction (Eq. (9)) is endothermic and requires a large amount of external supply heat. The equilibrium composition of the SG depends on the reformer temperature (*T*) and pressure (*P*), as well as the feed composition of the PT-steam mixture expressed by the steam to carbon molar ratio (*S/C*).

The *S/C* ratio is given by Eq. (10) [37].

$$\text{Steam-to-carbon ratio} = \left(\frac{\text{moles of steam}}{\text{moles of PT}} \right) \bigg/ \left(\frac{\text{moles of steam}}{\text{moles of PT}} \right)_{\text{stoichiometric}}$$

$$= \frac{(\text{moles of steam})}{104.4 \times (\text{moles of PT})} \quad (10)$$

This investigation was performed at atmospheric pressure because previous investigations of SR of oxygenated hydrocarbons have already shown that low pressures are thermodynamically preferable [43,44].

During the thermodynamic investigation H₂ production by SR of PT, the composition of the SG is determined using a simulation to minimize the Gibbs free energy using the Aspen Plus™ 10.2 software [40]. The R-Gibbs reactor (Aspen Plus™, 1988) is selected for the calculations using the UNIF-LBY equation of state [40]. In fact, minimization of the total Gibbs free energy is a suitable method to calculate the equilibrium compositions of any reacting

Table 1
Main components and average molecular composition of poultry tallow [38].

	Tripalmitin	Tristearin	Trioleate	Trlinolein	Trimyristin
Formula	C ₅₁ H ₉₈ O ₆	C ₅₇ H ₁₁₀ O ₆	C ₅₇ H ₁₀₄ O ₆	C ₅₇ H ₉₈ O ₆	C ₄₅ H ₈₆ O ₆
Composition (% mol)	26	10	41	21	2
Average molecular composition		C _{55.2} H _{101.42} O ₆			

system. This is based on the fact that the reaction system is thermodynamically favored when its total Gibbs free energy, expressed as a function of pressure, temperature and component concentrations, is at its minimum value [45]. The theoretical bases of this method are the same as that introduced in previous publications [33,36] and were also introduced in detail by other groups [2,37,43].

Depending on the catalyst employed and the completeness of conversion, the product distributions in the SG, through SR reaction, may be very complex. Accordingly to a previous study of beef tallow reforming [36], it is showed that all triglycerides are fully converted and the formation of by-products such as alkanes containing two or more carbon atoms, alkenes, acids and various alcohols are negligible. Consequently, the species considered in this work include only H_2 , CO , CO_2 , CH_4 and H_2O . The problem of carbon deposition is not posed in this paper because all of the considered configurations have $S/C > 2$ and $T > 300$ °C. It is showed, previously, for beef tallow reforming [36] that coke is absent at temperatures above 300 °C and when the S/C ratio is above 1. Consequently, carbon (coke) is excluded from the component list as plausible product.

3. Design and simulation of PT-to-hydrogen process using Aspen Plus™

Aspen Plus™ software was employed to estimate the materials and energy used during PT steam reforming. The results from the process simulation were subsequently used as inputs data for life cycle inventory.

A typical reforming based processor is constituted by a reforming unit coupled by a CO cleanup section introduced to guarantee H_2 production with a CO content compatible with PEMFC specifics. The cleanup of CO is performed by the WGS and the COPROX reactors [46]. In practice, the shift reaction takes place in two reactors: a High Temperature Shift reactor (HTS), operating between 573 and 673 K, and a Low Temperature Shift reactor (LTS), operating between 473 and 573 K [47]. The detailed flowsheet of the designed PT-to- H_2 process is depicted in Fig. 1.

Before being fed to the reforming reactor, the PT is preheated at 353 K (stream 1 → stream 2) and the water is heated and vaporized (stream 3 → stream 7). First, water (stream 3) recovers the calories from the produced synthesis gas (3 → 4) and then passes through the LTS cooler (COOL-LTS) (4 → 5), the HTS cooler (COOL-HTS) (5 → 6) and finally the SG cooler (COOL-SYNG) (6 → 7). The SG leaving the reformer is cooled to 573 K (HTS inlet temperature) in a heat exchanger (COOL-SYNG) (8 → 9). The product stream exiting the HTS reactor is cooled to 473 K (LTS inlet temperature) in COOL-HTS (10 → 11). The gas leaving the LTS reactor passes through a heat exchanger (COOL-LTS) before being fed to the COPROX reactor at 423 K (12 → 13). The gas exiting the COPROX reactor is finally cooled to 423 K after passing through a heat exchanger (COOL-CO) (14 → 15). The reforming, the WGS (HTS and

LTS) and COPROX reactors are modeled using the library model RGibbs. Therefore, the library model RGibbs reactor in the Aspen package is used to calculate the chemical and phase equilibria by minimizing the Gibbs free energy. The Aspen Plus™ library model HEATX is used for all of the heat exchangers with two input and output streams (i.e. COOL-SYNG, COOL-HTS, COOL-LTS and COOL-CO), whereas the PT pre-heater (PT-Preheat) is modeled using HEATER model.

To evaluate the energetic performance of the process we use the thermal efficiency. The thermal efficiency is based on considerations of the first law of thermodynamics and is calculated as the energy output divided by the energy input [48] as shown in the following equation:

$$\eta_{\text{Thermal}} = \frac{m_{H_2} \times LHV_{H_2}}{m_{PT} \times LHV_{PT} + Q_{PT-Preheat} + Q_{Reformer}} \quad (11)$$

where m_i and LHV_i are the mass flow and the Lower Heating Value of species i , respectively and Q_i the heat supplied to the equipment i .

4. Environment impact assessment via LCA methodology

4.1. LCA methodology

The methodology for this LCA of the PT-to- H_2 system has followed the guidelines set out by ISO14040-14043 [49]. The LCA methodology consists of four steps:

1. Goal and scope definition: specifies objectives of the investigation, the system boundaries (SB), and sets a functional unit (FU) to provide a reference for the inputs and outputs data.
2. Life cycle inventory (LCI) analysis: identifies energy and material inputs and outputs for all processes within the boundaries of the system.
3. Life cycle impact assessment (LCIA): evaluates the environmental impacts of the material and energy flows identified in the LCI analysis in three steps: (i) classification of impact categories, (ii) characterization of inventory data by quantifying their contributions to the impact categories, (iii) normalization and weighting.
4. Interpretation: evaluates the LCA model by identifying significant issues based on the results of LCI and LCIA, considering completeness and consistency and making conclusions and recommendations.

4.2. LCA of PT-to- H_2 system

4.2.1. Goal and scope definition

4.2.1.1. Goal and scope. The objective of this LCA is to evaluate the life-cycle environmental and energy performance of a H_2 production system based on SR of PT.

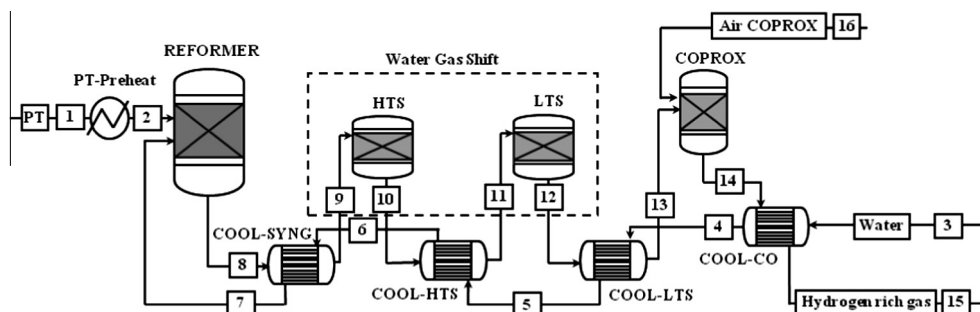


Fig. 1. A detailed flowsheet of the PT-to- H_2 process. Label numbers, 1 and 2: PT, 3–7: water, 8–15: synthesis gas, 16: air COPROX.

4.2.1.2. Functional unit, system boundary, and common assumptions. The FU chosen is one kg of H₂ produced. All emissions, materials and energy consumption and transport are based on this FU.

The SB, shown in Fig. 2, encompasses all the processes necessary to deliver the system's FU. The SB included rendering and reforming processes along with the required transportation processes. Rendering is a complex process that dries slaughter waste (poultry by-products) and converts it into purified fats (PT) and a protein meal [50]. The SB encloses all the processes indirectly embrace in the evaluated systems (background processes) such as: thermal energy production (for rendering and reforming processes), transportation, electricity production and water supply. The transportation implies the transport of raw material (poultry by-products) to the rendering process and the transport of PT to the reforming process. This study assumed that the average distance of both configurations (transport poultry by-products and transport of PT) is 100 km. The effect of transport distance on the system performance was studied in the sensitivity analysis. It should be noted that the construction and decommissioning phases and the manufacture and recycling of reforming catalysts are not considered in this study.

4.2.2. Life cycle inventory (LCI) analysis

The reforming data are derived from the process simulation in Aspen Plus™, whereas the rendering data are adapted from the inventory assessment of biodiesel production from poultry fat previously undertaken by López et al. [30]. The environmental consequences of the background process frequently account for a major portion of the total environmental burden identified in product LCA, across a broad variety of product types and a range of impact categories. In this work, the data of the background processes are taken from the ecoinvent database [51]. To reproduce the Tunisian electricity mix (not included in the SimaPro databank), the electricity production is introduced by fuel (97% from natural gas and 3% hydro).

4.2.3. Life cycle impact assessment (LCIA)

The LCI data was implemented into SimaPro 7.3 [52] to carry out the LCIA. The environmental impact categories quantified in this analysis were global warming (GWP), abiotic depletion (ADP), acidification (AP), eutrophication (EP), ozone layer depletion (ODP), photochemical oxidant formation (POFP), and cumulative non-renewable fossil and nuclear energy demand (CED). Except CED which is computed according to Hischier et al. [53], all other impact categories are evaluated by using the problem-oriented (midpoint) approach, CML baseline 2000 method [54].

5. Results and discussion

5.1. Chemical reaction investigation

The effect of temperature on H₂ yield (moles H₂ produced/kg PT in feed) at different S/C ratios is shown in Fig. 3.

The amount of H₂ produced at temperatures below 400 °C is relatively low compared to that at 650 °C. The H₂ yield increases with increasing temperature, reaches a maximum, and then decreases slightly. This behavior is the result of inhibition of the exothermic WGS (Eq. (2)) and methanation (Eqs. (3) and (4)) reactions. This is because of the fact that SR (Eq. (9)) reaction is endothermic and the equilibrium shifts towards the product side with increasing temperature, resulting in increased H₂ yield. The WGS (Eq. (2)) and methanation (Eqs. (3) and (4)) reactions on the other hand are exothermic, and the equilibrium shifts towards the reactant side (consumption of H₂) with increasing temperature. Fig. 3 shows that the H₂ productivity increases as the S/C ratio increases. This behavior is

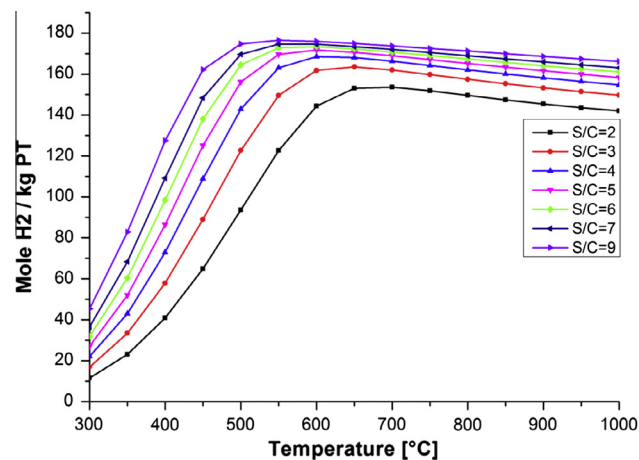


Fig. 3. Moles of H₂ produced per kg of PT as a function of temperature and S/C ratio at atmospheric pressure.

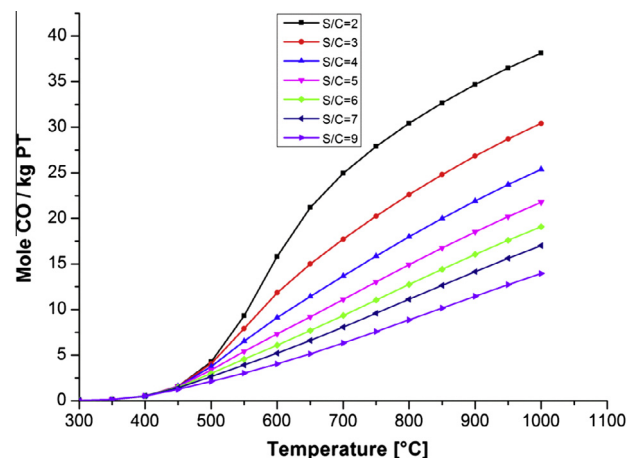


Fig. 4. Moles of CO produced per kg of PT as a function of temperature and S/C ratio at atmospheric pressure.

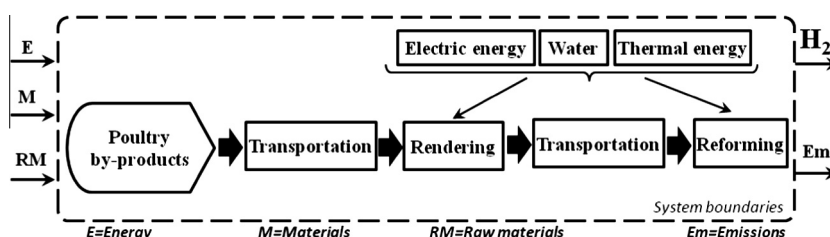


Fig. 2. Overview of the LCA boundaries of the PT-to-H₂ system.

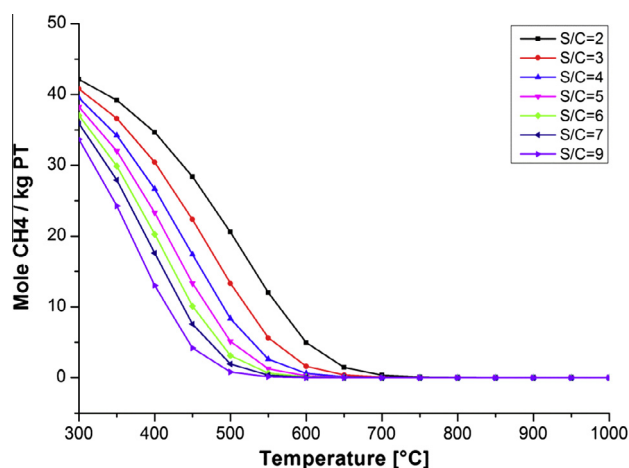


Fig. 5. Moles of CH₄ produced per kg of PT as a function of temperature and S/C ratio at atmospheric pressure.

Table 2
Mass and energy balances of PT-to-H₂ process.

	Value	Unit
<i>In</i>		
PT	2.78	kg/kg H ₂
Water	30.40	
Air	0.05	
Q _{Reformer}	99.84	MJ/kg H ₂
Q _{PT-Preheat}	0.24	
<i>Out</i>		
H ₂	1	kg/kg H ₂
H ₂ O	24.35	
CO ₂	7.84	
CO	0	
O ₂	0	
N ₂	0.06	
Thermal efficiency (%)	56.16	

Table 3
Main inventory data for the production of hydrogen (1 kg) via SR of PT system.

	Value	Unit
<i>Input</i>		
<i>Materials</i>		
PT	2.78	kg
Water	30.40	kg
<i>Energy</i>		
Thermal energy (rendering)	21.94	MJ
Electric energy (rendering)	0.85	kW h
Thermal energy (reforming)	100.08	MJ
Transport by lorry		
To rendering plant	1.32	tkm
To reforming plant	0.28	tkm
<i>Outputs</i>		
<i>Products</i>		
H ₂	1.00	kg
<i>Emissions</i>		
CO ₂	7.84	kg
H ₂ O	24.35	kg
CO	0.00	kg

Table 4
Environmental characterization results for 1 kg of H₂ (CML baseline 2000 method).

Impact category	H ₂ -Process	Electricity	Thermal energy	Transport	Total
GWP (kg CO ₂ eq)	5.03×10^{-4}	0.63	8.39	0.89	9.90
ADP (g Sb eq)	1.16×10^{-3}	5.73	73.48	6.50	85.71
AP (g SO ₂ eq)	6.25×10^{-5}	1.13	0.88	0.43	2.44
EP (g PO ₄ ³⁻ eq)	1.19×10^{-5}	0.03	0.08	0.09	0.20
ODP (mg CFC-11 eq)	2.18×10^{-5}	0.00	0.55	0.14	0.70
POFP (g C ₂ H ₄ eq)	4.36×10^{-4}	0.04	0.07	0.02	0.13
CED (MJ eq)	2.70×10^{-3}	11.94	140.66	15.01	167.61

consistent with Le Chatelier's Principle, which states that if a dynamic equilibrium is disturbed by changing the operating conditions, the position of equilibrium shifts to counteract the change. With an increase in S/C, the number of moles of water on the reactant side of Eqs. (2) and (9) increases, and hence the equilibrium of SR and WGS shifts towards the products side, resulting in increased H₂ productivity. The gain in H₂ yield is not significant for values of the S/C ratio above 5, whereas the reaction system consumes excessive amounts of water.

The effect of temperature on CO content in SG at different S/C ratio is shown in Fig. 4. At low temperature, the CO content was found to be quite low and increases with increase in temperature. This is because of the fact that the low temperature favors exothermic WGS reaction leading to low CO production. At higher temperatures ($T > 700$ °C), the carbon monoxide content strongly increases, which can be attributed to the thermodynamics of the WGS (Eq. (2)) reaction. As observed from the Fig. 4, the CO content decreases with an increasing S/C ratio because of an increase in the WGS reaction with S/C ratio.

For H₂ production, it is apparent that CH₄ is not a desirable product because the formation of CH₄ competes with H₂ yield. The CH₄ production was found to be very high at low temperature and decreased with increase in temperature as observed from the Fig. 5. This is because of the fact that the methanation (Eqs. (3) and (4)) are exothermic reactions and favors at low temperature. The CH₄ production was also found to decrease with increase in S/C ratio.

In conclusion, simultaneously achieving a high H₂ yield and a low CO content is not possible because the temperature must be high enough to obtain a reasonable H₂ production but the temperature must be as low as possible to minimize the CO content. The SG composition that maximizes H₂ production while minimizing the CH₄ and CO contents can be achieved at reforming temperatures of approximately 650 K and S/C ratio of approximately 5. With this condition, H₂ yield of 170.6 mol/kg PT and a CO concentration in the synthesis gas of 3.9% with a trace content of CH₄ (0.03%) can be obtained. These optimal conditions are, subsequently, used in the design and simulation of the entire PT-to-H₂ process.

5.2. Process simulation

Table 2 summarizes the mass and energy balance of the PT-to-H₂ process. These simulation results are expressed per kg of H₂ produced by the process. The thermal efficiency of the process is 56.16%, which indicates that approximately half of the energy fed to the process is recovered in the useful product (H₂). It should be noted that the thermal efficiency of the process is relatively lower than those cited in the literature and relative to other reformates (methane: 68% [55], ethanol: 79.4% [56] and methanol: 56.7% [57]). This difference is mainly attributed to the high consumption of thermal energy by the PT-to-H₂ process (100.08 MJ/kg H₂).

5.3. LCA results

Table 3 gathers the main inventory data of the PT-to-H₂ system. These data constitute themselves a key outcome of this investiga-

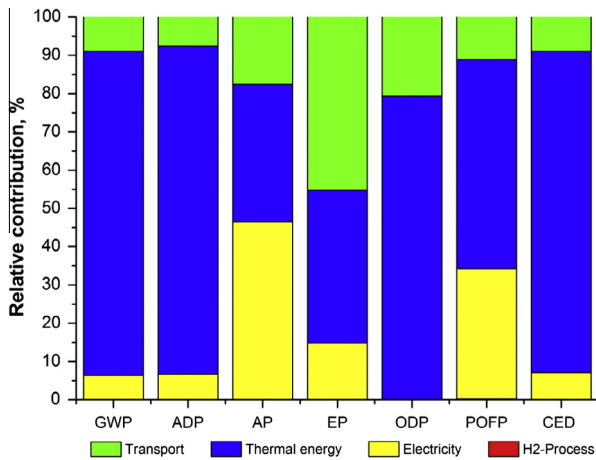


Fig. 6. Relative contribution of each life cycle stage to the environmental impact categories.

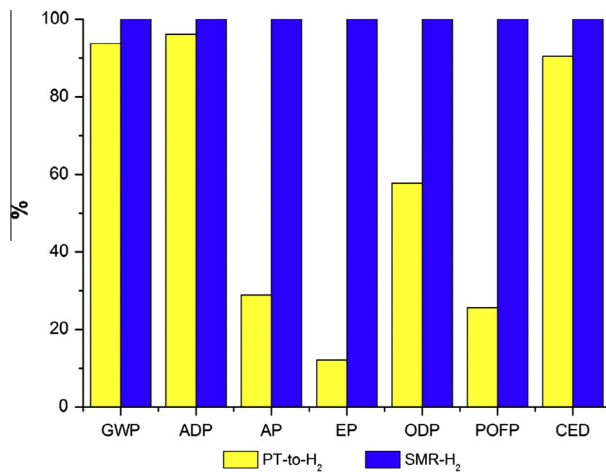


Fig. 7. Relative comparison of the environmental impacts of PT-to-H₂ and SMR-to-H₂.

tion. As it can be observed, inputs refer mainly to the rendering and reforming processes as well as to the electric and thermal energy requirements.

The characterization results computed for the production of 1 kg of H₂ are presented in Table 4. The contribution of the different subsystems (stages) involved in the PT-to-H₂ system is broken down so that top environmental impact contributors could be identified. Fig. 6 illustrates the relative contributions of each life cycle stage to the environmental impact categories.

The analysis revealed that thermal energy system is a major cause of the environmental burdens in the PT-to-H₂ system (highest impact in 5 of the 7 categories). Thermal energy involves the thermal energy demand for (i) rendering, and (ii) reforming. Approximately 82% of heat requirement impact is attributed to the thermal energy demand in the reforming process. Hence, environmental improvements should be focused on the minimization of this energy requirement.

As global warming and energy indicators are core concerns when assessing the performance of biofuel systems [26,58], the result interpretation and sensitivity analysis will mainly focus on GWP and CED. The GWP quantifies the contribution of gaseous emissions from the H₂ production system to the environmental problem of climate change. Table 4 shows that one kg of H₂ produced via PT-to-H₂ system creates about 9.90 kg CO₂-eq. The thermal energy requirement is responsible for 85% of contributions to GWP, especially due to the high consumption of heat in the reforming process (corresponding to approximately 70% of total GWP impact of the system).

The CED is especially suited to determine and compare the energy intensity of processes, including the direct as well as the indirect uses of energy. CED is used to investigate the energy use throughout the life cycle of H₂ and to identify most energy intensive steps of its production. As described in Table 4, a total of 167.61 MJ-eq is required to produce one kg of H₂. Fig. 6 shows that the contributors to CED are the thermal energy requirement, electricity consumption and transport operation by about 84%, 7% and 9% respectively.

The total energy output of PT-to-H₂ system is 120 MJ (LHV of H₂ produced). The total energy input is computed as the sum of non-renewable energy input is 167.61 MJ/FU (CED given by Table 4) and the renewable energy input mainly assigned to PT

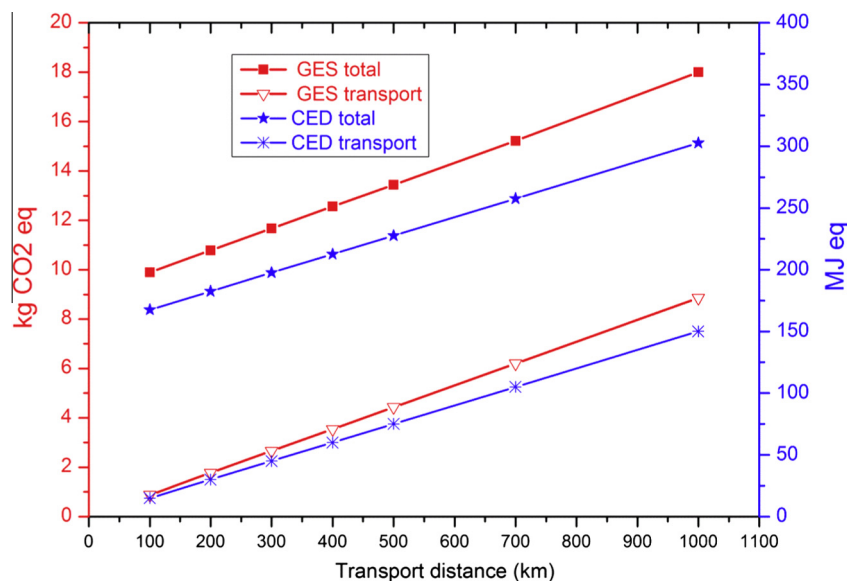


Fig. 8. Influence of transport distance on GWP and CED.

($m_{PT-LHV_{PT}} = 113.60 \text{ MJ/FU}$, m_{PT} is the mass of PT required to produce 1 kg H_2 (given in Table 3)). The total energy input is 281.21 MJ/FU. The overall efficiency of the system defined as (Energy of H_2 fuel/Total energy input) [59] is about 42.67%. To determine renewable character of the produced H_2 , we use the renewability ratio defined by Neelis et al. [59] and given by the following equation:

$$\alpha_{H_2, \text{ renewability}} = \frac{(\text{renewable energy input})}{(\text{renewable energy} + \text{non-renewable energy input})} \quad (12)$$

The renewability ratio of H_2 produced by PT-to- H_2 system is 40.40%. This low value is attributed to the high consumption of non-renewable energy through the life cycle of H_2 production: thermal energy production, electricity generation and transport.

In Fig. 7, the environmental profiles of PT-to- H_2 and conventional SMR for H_2 production (SMR-to- H_2) [29] are compared. PT-to- H_2 system is found to be a better option in terms of all impact considered. However GWP, ADP and CED remain relatively high, due to the excessive consumption of thermal energy.

In the base case, 100 km was taken as the average distance for transport. To determine the impact that transportation distances have on the study results, distances for transportation were varied in seven simulations (1: 100 km; 2: 200 km; 3: 300 km; 4: 400 km; 5: 500 km; 6: 700 km and 7: 1000 km). Fig. 8 illustrates the influence of transport distance on GWP impact and CED.

As shown in Fig. 8, the increase in transport distance increases significantly the GWP impact and CED. In fact, increasing transport distance leads to higher demand of diesel used in lorries. Obvious consequences of the increasing use of diesel are the increase in CO_2 emissions and in overall energy requirement. Consequently, it is important to note that transport distances should be kept short to reduce the environment damage as well as to reduce the financial burden of H_2 production.

6. Conclusion

In this research, various assessment tools are applied to comprehensively investigate PT-to- H_2 system. These tools investigate the chemical reactions, design and simulate the entire H_2 production process, study the energetic performance and perform an environment impact assessment using LCA methodology. LCA is applied to estimate environmental impacts in seven relevant impact categories: GWP, ADP, AP, EP, ODP, POFP and CED. The LCA results are subject to a systematic sensitivity analysis and compared to those calculated for H_2 production from conventional SMR.

The following conclusions can be drawn from the obtained results:

- The optimum conditions for the SR of PT, determined for maximizing H_2 production while minimizing the CH_4 and CO contents, can be achieved at reforming temperatures and S/C ratio of 650 K and 5, respectively.
- The thermal efficiency of the designed process is 56.16%; this efficiency is lower than those cited in the literature and relative to other reformates (methane, ethanol and methanol). This difference is mainly attributed to the high consumption of thermal energy by the process (100.08 MJ/kg H_2).
- One kg of H_2 produced via PT-to- H_2 system creates 9.90 kg CO_2 -eq and requires about 167.61 MJ-eq as primary energy consumption.
- Thermal energy production process was the main contributors to the selected environmental impact categories. Improvement actions to minimize the reforming thermal energy are strongly recommended.

- Transport distance should be minimized to enhance the environmental performances of the system.

Finally, this study is part of ongoing work related to research and development of bio-renewable H_2 production. The results indicate where effort needs to be deployed to improve the technology performance and process design which can help in lowering the environmental impacts in the whole life cycle. Moreover, it is imperative that engineers, scientists and stakeholders involved in green energy and technologies include both thermodynamic and LCA considerations in their panel of environmental, social and economic impacts for decision making.

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